Rapid Determination of Chloride Concentration of Cheese by Use of a Pungor Electrode

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Abstract

When a silicone membrane containing ion exchange granules charged with chloride ion separates an homogenate of cheese in water from a standard potassium chloride solution, a membrane potential is developed proportional to the chloride ion concentration in the homogenate. This effect can be used to determine the chloride concentration in cheese by use of a conventional pH meter equipped with a commercially available chloride electrode. Good agreement was found between results obtained by this method and the standard Volhard titration. The new method proved superior to the direct potentiometric determination of chloride in cheese by using a silver–silver chloride electrode.

The sodium chloride content of cheese influences both flavor and flavor stability. Processing conditions can influence the salt content; therefore, it is important to monitor the salt level in the finished product, particularly when developing new cheese types. A modification of the standard Volhard procedure, both tedious and time-consuming, has been the method of choice, since apparently no other satisfactory method has been develoed. Anderson (1) has described a method which should permit the direct quantitative potentiometric determination of chloride in cheese by use of a silver–silver chloride combination electrode in conjunction with a standard pH meter. However, the data he presents contain the analysis of only a single cheese and there are no further reports of its use.

The recent commercial development of a chloride specific membrane electrode, based on research of Pungor et al. (5), suggested a new method, less time-consuming than the Volhard procedure, for the quantitative determination of chloride in cheese.

Our paper describes a simple method for determining the chloride content of cheese, using this new electrode, and shows a comparison of results obtained by use of the Volhard procedure, the silver–silver chloride electrode, and the ion exchange membrane electrode.

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Experimental Procedure [1]

Cheeses used in our experiments were commercial Cheddar and Cottage tyes bought at local supermarkets and experimental low-fat Cheddar types produced in our laboratory (3).

The cheeses were prepared for analysis as follows: A slice was taken from the center of the cheese to be analyzed, diced, and an approximately 5-g sample quickly weighed into a Tenbroeck tissue grinder. Ten grams distilled water were added and the mixture homogenized until a lump-free purée was obtained. Gentle heating prior to grinding speeded emulsification. A weighed 2-3-g aliquot of the emulsion was pipetted into a 100-ml volumetric flask. Five milliliters boiling 0.1 N sodium hydroxide were added, to further disperse the mixture. The sample was diluted to volume with 0.1 N nitric acid and allowed to equilibrate at room temperature before reading. This mixture could be used for the direct potentiometric determination of chloride, using both the silver–silver chloride electrode and the ion exchange membrane electrode, thus permitting a relatively simple comparison of results.

The ion exchange membrane electrode was obtained from National Instrument Laboratories, Rockville, Maryland, and used in conjunction with a standard calomel electrode and a Fisher Accumat pH meter or a Radiometer pH meter. All readings were made on the millivolt scale.

Electrode performance was calibrated using standard solutions of sodium chloride with concentrations ranging from 0.01 to 1.0 mg/ml. This concentration range proved to be the most convenient for the size of cheese samples employed.

A no. 39187 Silver Billet Combination Electrode, electrolytically coated with silver chloride according to manufacturers' instructions, was obtained from Beckman Instruments, Inc., Fullerton, California.

[1] Reference to certain products or companies does not imply an endorsement by the Department over others not mentioned.

The official Volhard procedure for determination of chloride in cheese was followed (4).

Results

The logarithmic relationship between the electromotive force (emf) measured using an ion exchange membrane electrode and the salt concentration in simple aqueous solutions is shown by the calibration curve in Fig. 1.

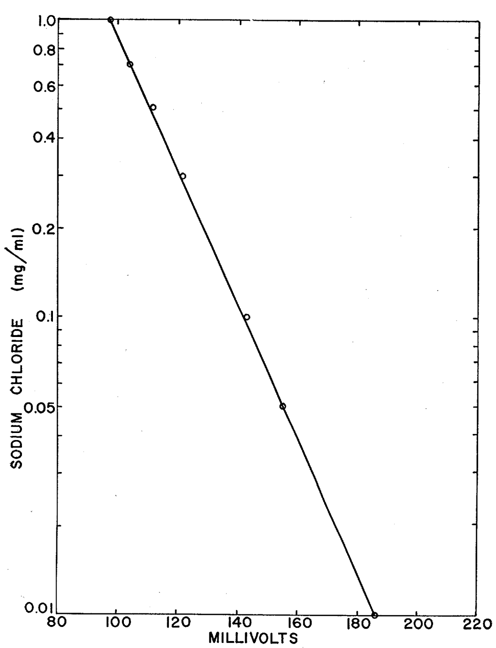

FIG. 1. Calibration curve for the membrane electrode. Potentials measured at room temperature vs. a saturated calomel electrode.

Effect of temperature on the emf is shown by the data in Fig. 2. Considerable error can occur in readings taken without temperature compensation, whereas little or no drift occurs over a wide temperature range when readings are made with a temperature compensator attached to the pH meter. Temperature effects can also be avoided by carrying out all work in a constant temperature room.

Table 1 demonstrates that the performance of the ion exchange membrane electrode is not affected by wide variations in pH.

Seventeen samples of experimental low-fat Cheddar type cheeses were analyzed in duplicate, using the silver–silver chloride electrode, the ion exchange membrane electrode, and the Volhard procedure. Fig. 3 shows the relationship between the chloride concentrations in these cheeses as determined by the Volhard procedure and the silver–silver chloride electrode. The wide scatter indicated great disagreement between these methods; the calculated correlation coefficient was 0.31.

Fig. 4 shows a plot of the data obtained by use of the Volhard procedure and the ion exchange membrane electrode. Nineteen samples of commercial Cheddar and Cottage cheeses were analyzed in duplicate in addition to the 17 samples of low-fat Cheddar type cheeses mentioned above. Regression analysis provided the line drawn through the points. The correlation coefficient was found to be 0.96.

Discussion

The general form of the ion exchange membrane electrode, as shown in Fig. 5, was used in our studies. The body of the electrode is filled with a standard potassium chloride solution of appropriate concentration; the membrane across the bottom of the tube, consisting of close-packed particles of ion exchange resin in the chloride form embedded in a silicone rubber matrix, separates this solution from that of the sample.

The detailed mode of operation of an ion exchange membrane electrode is not fully understood. However, the magnitude of the membrane potential can be measured using a conventional pH meter equipped with a standard calomel reference electrode.

Pungor (5) found that when the common ion in the membrane was locally bound in concentrations that could be considered extremely high, the situation could be expressed mathematically; he based his considerations on the reduced form of the Teorell equation shown below:

$$E = \frac{RT}{F} ln \frac{a_1}{a_2}$$

where E = membrane potential

R = gas constant

F = Faraday number

T = absolute temperature

a_1, a_2 = mean activity of ions on both sides of the membrane.

This equation describes the membrane potential developed by selective membranes. In this simplified form, the membrane potential is directly proportional to the absolute temperature and to the logarithm of the ratio of the concentration of the mean ion activity on both sides of the membrane. On the basis of this, the observed potential should be affected only by the temperature and the difference in ion activity across the membrane.

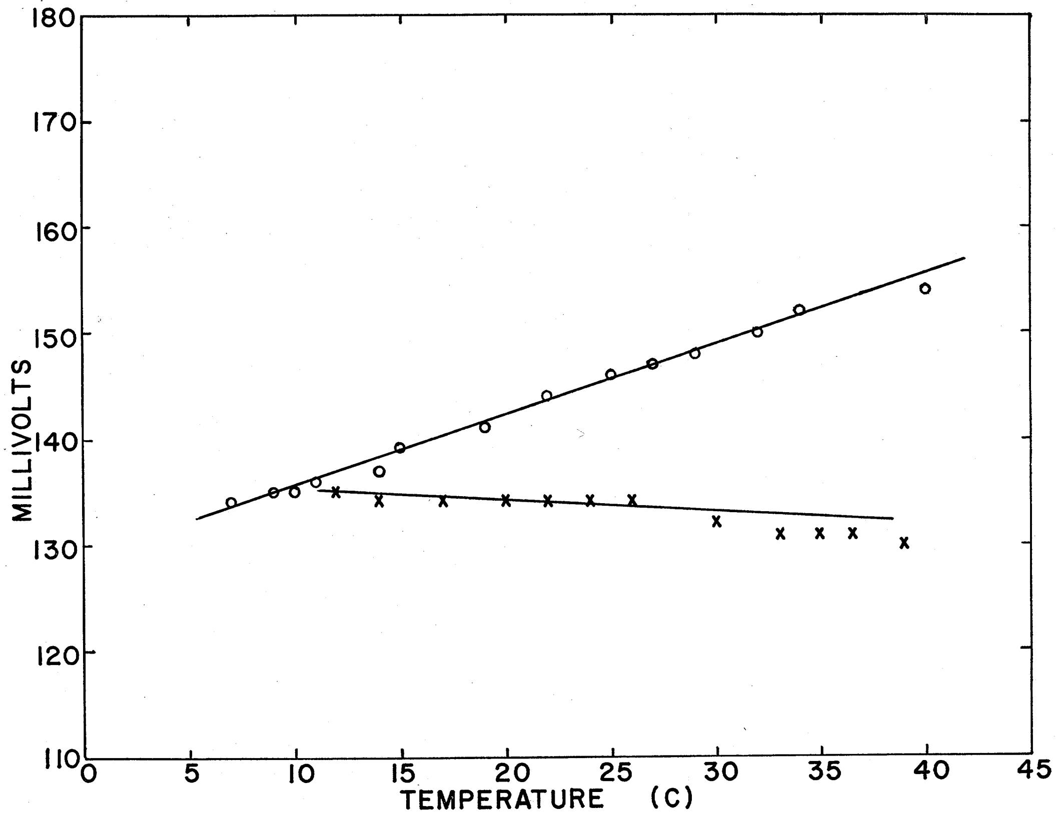

FIG. 2. Effect of temperature on the potential of a solution containing 0.1 mg/ml sodium chloride.
o————o: Without temperature compensation
x————x: With temperature compensation

TABLE 1

Response of chloride membrane electrode to solutions of different pH, containing 0.1 mg/ml sodium chloride

Solution	pH	Potential (mv)
0.1 N Nitric acid	0.50	140
0.1 N Phosphate buffer	4.45	140
0.1 N Phosphate buffer	5.98	140
0.1 N Phosphate buffer	6.50	142
0.1 N Phosphate buffer	7.00	140
0.1 N Phosphate buffer	7.50	144
0.1 N Phosphate buffer	7.98	142
0.1 N Phosphate buffer	8.98	142

Rechnitz and Kresz (6) have studied the selectivity characteristics of chloride and bromide type membrane electrodes; these studies demonstrate that the response of the chloride membrane electrode is affected by the presence of bromide and iodide ions, but response to inert anions such as sulfate, nitrate, and perchlorate is negligible.

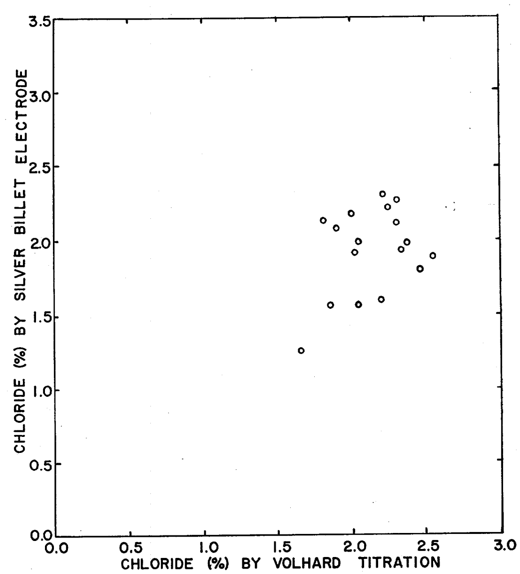

FIG. 3. Comparison of the determination of chloride by the Volhard procedure and by the silver billet electrode.

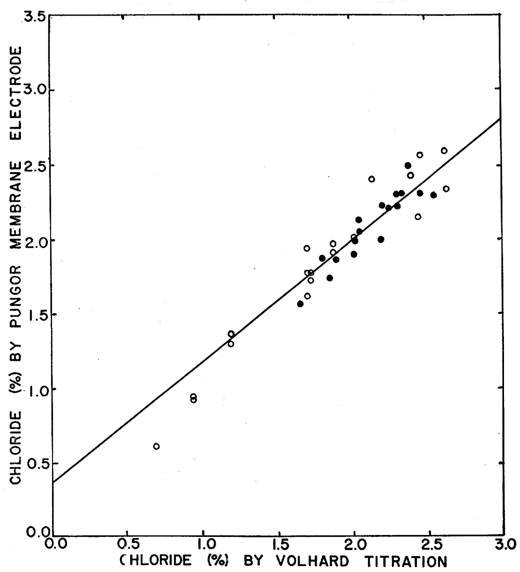

FIG. 4. Comparison of the determination of chloride by the Volhard procedure and by the Pungor membrane electrode.

Solid circles represent low-fat Cheddar type cheeses also analyzed by the silver–silver chloride electrode as shown in Fig. 3.

Open circles represent commercial Cheddar, Cottage, and additional low-fat Cheddar type cheeses.

According to manufacturers' specifications, the response of our electrode would be affected by hydroxyl ion concentration greater than 0.02 M. It can be seen from Table 1 that electrode response to a series of solutions of different pH containing the same amount of sodium chloride remains unchanged.

Rechnitz and Kresz (6) also studied the dynamic response behavior of the membrane electrodes and found that potentiometric titrations and equilibrium potential measurements are influenced by somewhat slow equilibration (1-3 min) of the membrane electrodes to changes in halide concentration. The electrode we used, however, stabilized within 15 sec and did not vary more than ± 1 mv over a period of several minutes at constant temperature, well within manufacturers' specifications.

Rechnitz and Kresz made no study of the effect of temperature on the membrane electrode response but, as shown in Fig. 2, temperature fluctuations cause serious error in electrode response. This is to be expected in view of the requirements of the Teorell equation. We found that results reproducible to ± 2 mv could be obtained with careful temperature control.

The highest sensitivity of the silver billet combination electrode is achieved with the thinnest possible coating of silver chloride on the tip; this sensitivity decreases rapidly when the coating changes color from violet to black with age or is partially dissolved by the sample. In addition, accuracy of this electrode is seriously affected not only by temperature but also by slight variations in pH. To obtain good results using this electrode, it is necessary to maintain a constant, highly acidic pH to avoid interference by carbon dioxide dissolved in the sample to be analyzed.

Fig. 3 compares results obtained by use of this electrode to those obtained by the Volhard procedure. Statistical evaluation of these data by linear regression analysis (2) conclusively demonstrates that the margin of error occurring with use of this electrode is too great to show any relationship existing between results obtained by these two methods.

On the other hand, regression analysis demonstrates that a significant linear relationship does exist between results obtained by use of the ion exchange membrane electrode and the Volhard procedure. The line drawn through the points projected on Fig. 4 should ideally have a slope of one and an intercept of zero. The actual line deviates from this position for reasons which we did not investigate further, since the correlation coefficient was found to be 0.96, well within the figure anticipated from the electrode performance specifications.

From the data presented here, we have concluded that the ion exchange membrane electrode can be used for chloride analysis of cheeses with a comparatively good degree of accuracy and with a considerable saving of time, when compared to the Volhard procedure.

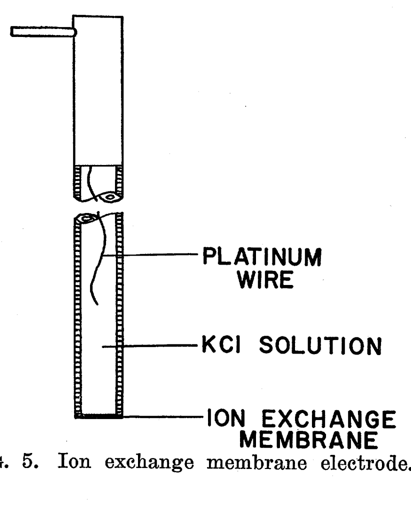

FIG. 5. Ion exchange membrane electrode.

Although good results are obtainable with a pH meter of the type employed here, greater sensitivity for small potential ranges would be provided by a meter with an expanded scale.

As the electrode is relatively new, we can make no statements regarding the durability of the physical and chemical characteristics of the membrane during extended use. However, by employing reasonable care in handling, the electrode should be an effective tool for routine determination of the chloride content of cheeses, when used as described. The method also speeds cheese analysis, since an aliquot of cheese homogenate can be used for fat determination.

Acknowledgments

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